Poly(epsilon-caprolactone) based polymer electrolytes and its application in Flexible solid supercapacitors

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Abstract

Supercapacitors can be used as stand alone or complement batteries and solar cells to form hybrid systems that provide high power density and ultra fast charge-discharge rate. Flexible solid supercapacitor have recently been developed indicating tremendous opportunities with this new generation solid energy storage devices because it is thin, light weight, flexible, low maintenance, minimize leakage and easy sealing processes. In this work, proton-conducting polymer electrolytes based on poly (epsilon-caprolactone) (PCL) containing ammonium thiocyanate (NH_4SCN), ethylene carbonate (EC) and succinonitril (SN) will be presented. The polymer membranes were prepared by solution casting. The potential of electrical double layer capacitors (EDLCs) fabricated from symmetry activated carbon electrodes and the PCL based films has been studied. The highest conducting samples show a room temperature ionic conductivity of 4.3 x 10^{-3} S cm^{-1}. The fabricated EDLC cells were preliminary evaluated by cyclic voltammetry studies. The highest specific capacitance of EDLC cell is found to be 27.7 F g^{-1} at scan rate 10 mV s^{-1}. Different cell designs will also be discussed.

Keywords: Polymer electrolyte, poly(ε-caprolactone), electrical double layer capacitor

1. Introduction

The utilization of eco-friendly materials as the component materials in electrochemical devices is a hot topic of research because it can minimize the toxic technological rubbish [7-1] left behind upon disposal. In this work, Poly(ε-caprolactone) (PCL) is used as polymer host in solid polymer electrolyte (SPE) system. PCL is an aliphatic polyester that is non-toxic as approved by FDA, biodegradable and has excellent biocompatibility and bio-resorbability. It has many applications in the bio-medical field [8, 9-2,3]. Furthermore, the low glass transition temperature, -60 °C of PCL containing an ester oxygen (Lewis base) that can coordinate cations [10, 11-4,5] making it a candidate as polymer host in SPE system.

Succinonitrile (SN) is an organic ionic plastic crystal (OIPC) electrolyte for many device applications because it has good thermal and electrochemical stability, high plastic mechanical properties, fast ion transport and is flexible in terms of chemical design. SN has high dielectric constant (around 55 at room temperature) making it a good organic solvent. The room temperature ionic conductivity values of SPE based on SN have been reported in the range between 10^{-4} to 10^{-3} Scm^{-1}. Those SPEs were added with various types of lithium or sodium salts. In this work, ammonium salt is used as the source of charge carriers.

Supercapacitors are considered as one of the energy storage system. It lies between batteries and conventional dielectric capacitors in terms of energy and power densities. It has wide applications such as portable mobile devices, computer power back-up, electronics and electric vehicles. One of the supercapacitors is electrical double layer capacitors (EDLCs). An EDLC usually consists of two porous activated carbon electrodes sandwiching an electrolyte [1, 2-6,7]. Activated carbons (ACs) are basic materials for EDLC electrode because it's structure is porous in nature, with high surface area, excellent adsorption property and high electrical conductivity. Upon charging and discharging of the cell, the charge carriers in the electrolyte will move to/away from the electrolyte-electrode interfaces [3, 4,-8,9] without actual charge transfer. This makes it a clean rechargeable energy storage system with high energy density, maintenance-free long cycle life operation and environmentally friendly technology [5-10].

The main objective of this work is to study the potential of flexible EDLCs fabricated from symmetry activated carbon electrodes and poly (ε-caprolactone) (PCL) based PE. SPE was prepared by solution casting. SN was incorporated to the highest conducting PCL-NH_4SCN-EC system as the additive to improve ionic conductivity. The temperature dependent conductivity and structural studies were carried out by impedance spectroscopy and XRD. The fabricated EDLC cells were preliminary evaluated by cyclic voltammetry studies.

2. Experimental procedure

2.1. Preparation of polymer electrolytes

PCL and ethylene carbonate (EC) (Aldrich) were used as received. Ammonium thiocyanate (NH_4SCN) (R&M Marketing) were dried in an oven at 45 °C for 24 h prior to use. SN was purchase from Sigma-Aldrich and used without further changes or purification. SPE contains of PCL, SN, EC and NH_4SCN were prepared by solution casting. Mixture of PCL-NH_4SCN (74:26) and EC were fixed at (50:50). Varying SN content is added to the mixture from 0 wt.% to 10 wt.%. The film's thickness was ranging from 100 to 150 μm. The optimized free standing SPE film was applied to fabricate EDLC cells.

2.2. Preparation of electrodes and EDLCs

The EDLC electrodes were prepared by doctor blade technique. A mixture of 80 wt% activated carbon (Kuraray Chemical Co. LTD., Japan), 5 wt% carbon black (Denka Black, Singapore), 5 wt% multi-walled carbon nanotubes (Aldrich, USA) and 10 wt% poly(vinylidine difluoride) (Aldrich) in 1-methyl-2-pyrrolidone (Merck, Germany) as solvent was stirred until the slurry become homogeneous. The slurry was then doctor-bladed on aluminum foils that were cut (area ~1.0 cm^2). The coated electrodes were then heated in an oven at 60 °C. The weight of each electrode was measured including the carbon black and binder, around 10 mg. EDLCs cells were fabricated by sandwiching the best conducting PCL-based SPE film between two EDLC electrodes for further studies.

2.3. Instrumentation

Structural studies of the SPE films were tested using XRD D5000 diffractometer at 40 kV, 40 mA and a scattering angle range from $2\theta = 5° - 80°$ with a step size of 0.1° at temperature 25 °C.

HIOKI 3531 Z LCR Hi-tester has been used to measure ionic conductivity of the PE films in the frequency range from 50 Hz to 1 MHz. The conductivity was measured by sandwiching the PE films between two stainless steel electodes.

The cyclic voltammetry (CV) of the EDLC cells were evaluated at scan rate 10 mV s^{-1} between a floating potential of -1.0 and 1.0 V. Both tests were using the PGSTAT12 potentiostat. The single electrode specific capacitance of the EDLC can be evaluated using equation:

Specific capacitance, $C_s = \frac{2i}{mv}$

where *i* is current in ampere, *m* is the mass of the single electrode in grams and *v* is the scan rate in volt per second.

3. Results and Discussion

3.1. Characteristics of Solid Polymer Electrolytes

In SPE system, the ion-ion interactions are a complicated subject and ion transport mechanism is not well understood yet. It was reported that ionic conductivity predominates in the environment with rich amorphous phase. In the current work, SN is added as organic plasticizer to PCL-based system in order to boost the ionic conductivity.

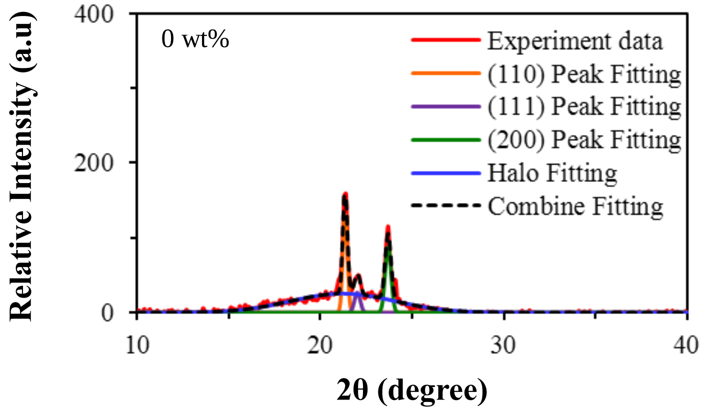

Fig. 1 Fitted XRD patterns of polymer electrolytes.

It is found that the addition of SN generates significant disorder into the polymer matrix, Figure 1. The orthorhombic PCL crystalline peaks at 2θ = 21.4°, 22.0° and 23.7° were deconvoluted from the amorphous spectrum centered around 2θ = 21.0° to calculate the degree of crystallinity, χ_C according to:

$$\chi_C = \frac{I_C}{(I_C + I_a)} \times 100\%$$

Here, I_C refer to the total crystalline peaks integrated intensity and I_a is amorphous integrated intensity of the halo.

Figure 2 displays the ionic conductivity of SPE as a function of SN content.

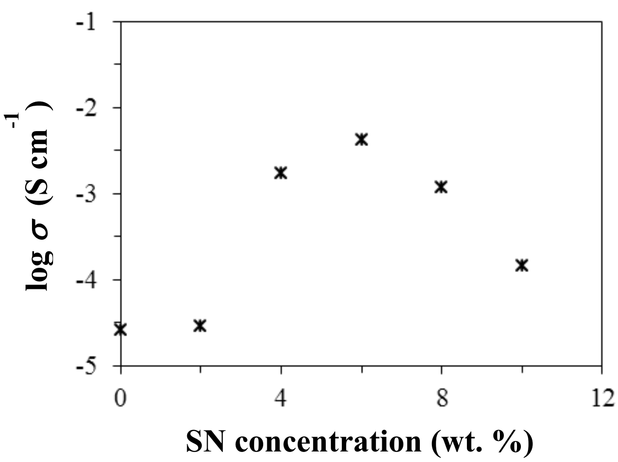

Fig. 2. Ionic conductivity of SPE as a function of SN content.

The addition of EC inhibit and disrupt the order/folding pattern of PCL polymer chain. Interactions between polymer-SN and ion-SN in PCL-NH_4SCN-EC-SN system manage to interrupt polymer-polymer interaction either by occupying or increasing inter and intra-chain separations [11]. Eventually, the ordered and rigid crystalline domains of PCL are disrupted increasing the disordered amorphous domains.

The increase in amorphousness is accompanied by the increase in conductivity. The room temperature ionic conductivity of PE increased from 3.8×10^{-5} S cm^{-1} to 4.3×10^{-3} S cm^{-1} of 6 wt.% SN. In the amorphous region, the polymer chains are irregular and entangled, leading to a loose molecular packing with smaller density. On the other hand, the polymer chains in crystalline region are arranged regularly with high density molecular packing. Hence, it is easier to move the polymer chain in amorphous state than in crystalline state.

3.2. Performance of EDLCs cells

The EDLC cell preparation is given in Figure 3.

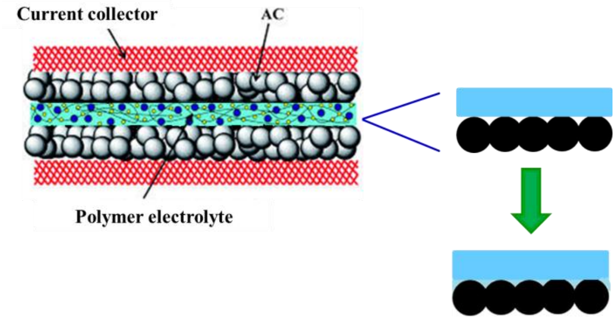

Fig. 3. The EDLC cell preparation with the best conducting solid polymer electrolytes

The charge storage at the electrode and electrolyte interfaces in the anodic and cathodic regions can be seen by CV of the EDLC cells. Fig. 4 shows the CV in the potential range of 0 V to 1.0 V at scan rate of 10 mV s^{-1}.

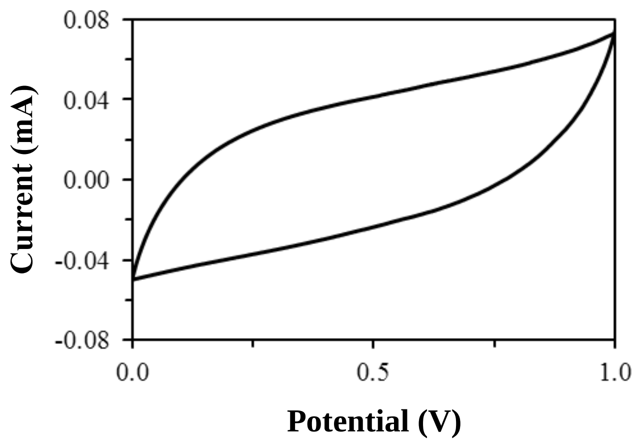

Fig. 4. Cyclic voltammogram of EDLC at scan rate 10 mV s^{-1}.

The CV curve obtained is deviated from a perfect rectangular shape. This could be attributed to the finite value of the equivalent series resistance (ESR) in the EDLC. The mirror image of the current responses about the x-axis shows a quite good symmetry. The cell specific capacitance of the EDLC is calculated to be 27.7 F g^{-1}.

4. Conclusions

The best conducting PCL-based flexible SPE membranes shows a room temperature ionic conductivity of 4.3×10^{-3} S cm^{-1} at 6 wt.% SN. From the XRD analysis, the addition of SN creates disorder into the PCL polymer matrix and therefore changes χ_C. The application as energy storage device (EDLCs) has been fabricated from symmetry activated carbon electrodes and PCL-based SPE. The cell specific capacitance of the EDLC is 27.7 F g^{-1}.

Acknowledgement

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